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ABSTRACT

Exact solution for scattering cross section coming from Xu's computations is compared with different approximations.

1 INTRODUCTION

Many industrial operations involve solid-liquid suspensions. During the corresponding processes suspensions are put in motion. As a consequence, collisions and sticking of particles, i.e aggregation of particles, occurs. This phenomenon is due to Brownian motion in the case of sub-micronic particles and due to the velocity field heterogeneity in the case of larger particles. The aggregates formed usually contain a few primary particles because large aggregates undergo fragmentation leading to a limit size for the aggregates. So, primary spherical particles of metallic oxides (ZrO_2, TiO_2, Al_2O_3, SiO_2) are used as precursors in ceramic industry. The corresponding suspensions contain aggregates, each one composed of less than one hundred primary particles. The on-line characterization of the suspension is made by spectral turbidimetry [1], i.e. attenuation of a light beam by particle scattering and absorption. In order to analyze the optical signal, i.e. turbidity, the scattering cross sections of aggregates are needed. An important literature is available about the calculation of the light scattering cross section of aggregates. For instance, Xu and Khlebtsov [2] (for more information see the references therein) proposed an exact calculation based on a generalization of the Mie theory. So, the scattering cross sections depend on the size of the primary particles, on the morphology of the aggregates and on the refractive index of the material and of the medium. This exact, but complicated theory cannot be easily used to interpret, for instance, turbidity spectra on-line. This is due to the time consuming calculations for a large amount of different aggregates (doublet, triplet...) which are produced during the aggregation process. The topic of this paper is to propose approximations (averaged over all the orientations) for scattering cross section corresponding to aggregates of few spherical and non absorbing particles. As the accuracy of turbidity measurements is more than 5%, we will consider an approximation as useful and valid if it describes the reality within this error.

2 SEVERAL APPROXIMATIONS FOR SCATTERING CROSS SECTIONS

An aggregate is composed of N primary spherical particles. The radius and the dimensionless size parameter of the primary particle are respectively denoted *a1* and $\alpha = \frac{2\pi}{\lambda_1} a_1$. Two kinds of modeling can be used to calculate approximately the optical properties of porous materials:

Effective refractive index method. An aggregate is characterized by its effective diameter $a_{N;e}$ and its mean inner volume fraction $\overline{\Phi a} = (N a_1^3)/a^3_{N,e}$. The easiest way to

determine the optical properties of an aggregate is to calculate its effective refractive index m_a (see, for instance, [3]). The equation derived by Maxwell-Garnett has been proved to be suitable in certain case

$$\frac{m_a^{\,2}-1}{m_a^{\,2}+2}=\overline{\Phi}_a\frac{m^2-1}{m^2+2}, \tag{1}$$

where m and m_a are the relative refractive index for primary particles and aggregates, respectively. With known diameter and effective refractive index of aggregate, the Mie theory [4] allows us to calculate the scattering cross section CN for a given wavelength. Two particular cases can be considered for choosing the effective diameter:

- ✓ the compact sphere: the non porous sphere with the same mass of material as in the aggregate. Thus,

$$a_{N;e} = N^{1/3}\ a_1\ (\overline{\Phi}a=1 \text{ and } m_a = m); \tag{2}$$

- ✓ the "projected area" equivalent sphere: in aggregation theory and optical properties modeling, the relevant parameter is the projected area S_p of the object on a plane. Thus, we define the radius $a_{N;e}$ of the equivalent sphere for an aggregate as:

$$\pi a^2{}_{N,e}=\left\langle S\,p\right\rangle_0, \tag{3}$$

where $\left\langle S\,p\right\rangle_0$ is the average projected area according to all aggregate orientations.

Soft-particle methods. Generally, the object (primary particle, aggregate ...) can be divided into smaller identical parts (elements). Each element is polarisable. In the presence of a variable electric field, the element becomes an oscillating dipole, which itself creates an electromagnetic field. When an object is illuminated by an electromagnetic wave, each element receives the incident electric field and the one coming from the other elements. As a result, one may associate an oscillating dipole moment to each element. Thus, the object emits an electromagnetic wave (scattered wave), which includes the contribution of each oscillating dipole.

Most often, the incident wave is randomly polarized and the object (scatterer) can randomly orientate. Thus, the optical properties are obtained after calculating an average over all the wave polarization states and object orientations.

Several models were published, each one characterized by the polarisable element, the object, the calculation type. For instance, Berry and Percival [5], Khlebtsov [6] and Xu and Khlebtsov [2] calculate the aggregate optical properties, if the polarisable element are respectively: Rayleigh scatterer, Rayleigh-Debye-Gans (RDG) scatterer and Mie scatterer.

So, the Khlebtsov's [6] procedure, similar to Berry-Percival one, has been applied to aggregates of many particles (fractal aggregates). RDG scatterers are characterized by $|m-1|<<1$ and $\frac{4\pi}{\lambda}a_1|m-1|<<1$. Then, the scattering cross section obeys:

$$C_N = N^2 D\int_{4\pi} F_1(\vartheta)S(q)d\Omega \text{ with } C_1=\int_{4\pi} F_1(\vartheta)d\Omega, \tag{4}$$

where Ω, ϑ, q are the solid angle, the scattering angle and the scattering vector, respectively. D is the contribution of the multiple scattering inside the aggregate [6].

$F_1(\vartheta)$ is proportional to the phase function corresponding to the primary particle (sphere). The structure factor *S(q)* depends on the aggregate morphology:

$$S(q) = \left[N + \sum_{i=j=1, i\neq j}^{N} \sin(qR_{ij}/(qR_{ij}) \right] / N^2 . \quad (5)$$

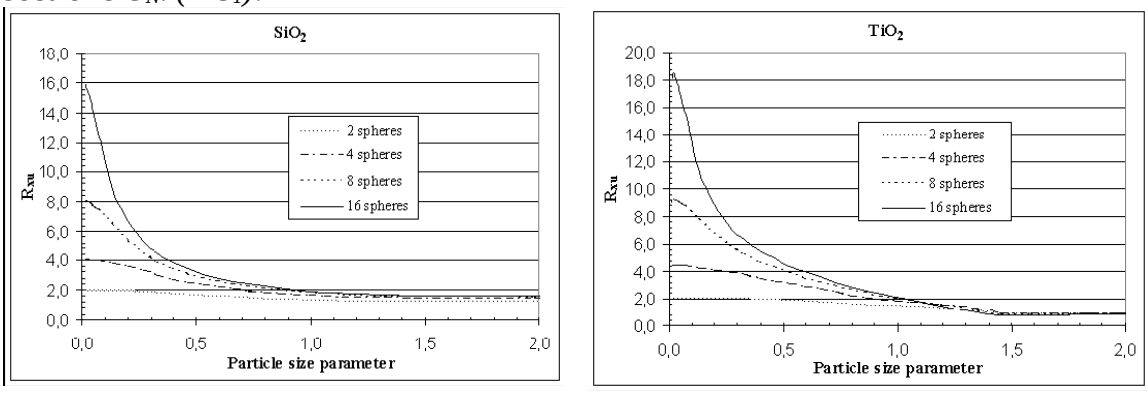
Here, $R_{i;j}$ is the distance between the centers of the primary particules *i* and *j* inside the aggregate. However, when $\frac{4\pi}{\lambda} a_1 |m-1|$ is not small, the approximation of anomalous diffraction [4] can be applied. In the Rayleigh-Debye-Gans domain, there is interference of electromagnetic waves which are independently scattered by all small volume elements. In the anomalous di_raction domain, there is straight transmission and subsequent diffraction. In this case, the scattered intensity is concentrated near the original direction of propagation and the scattering cross section obeys the relation [4]:

$$C_N = 2 \int \int_{[Sp]} (1 - \cos \frac{2\pi}{\lambda} \delta(m-1)) dS_p \quad (6)$$

Integration is performed over the object projected area S_p on a plane perpendicular to propagation direction. δ is the path of light through the object. This calculated path is a function of the projection coordinates. This kind of calculation was previously achieved for fractal clusters by Khlebtsov [7].

3 NUMERICAL INVESTIGATION

We studied aggregates with number of particles N = 2; 4; 8; 16; 64; 100. The size parameter of the primary particle is in the range [0.013 ; 9.25]. For each N-aggregate, we consider several morphologies or compactness: chain, plane, cube... Tested materials are the ones with low (SiO_2, m = 1.08), intermediate (Al_2O_3, m = 1.32) and high (TiO_2, m = 1.94) optical contrast in water. We compare exact values of scattering cross section derived from Xu's theory [2] with the corresponding one from the above-described approximations: compact sphere (CS) (Equations. (1), (2)); effective refractive index (ERI) method (Equations. (1), (3)); Percival-Berry-Khlebtsov (PBK) method (Equations. (4), (5)); anomalous diffraction (AD) approximation (Equation (6)). Results are shown as the ratio of actual scattering cross section to the sum of aggregate primary particles cross sections $C_N/(NC_1)$.



a b

Figure 1: R_{Xu} for linear configuration with N primary particles, case a):SiO_2, b):TiO_2.

Consider main features of mean scattering cross sections of aggregates like it was done in [8]. Figures 1(a,b) represent $R_{Xu} = C_{Xu,N}/(NC_{Mie,;1})$ against the primary particle size parameter for several N-chains and for the two systems TiO_2/water and SiO_2/water. The trends are the same for compact aggregates (the compact configuration means for example a tetrahedron for the case of 4 primary particles, a cube for the case of 8 and so on). The shape of the curves R_{Xu} is similar whatever the material. R_{Xu} is a decreasing function of the size parameter. For very small size parameter R_{Xu} tends to N as expected by [4]. For high value of the size parameter R_{Xu} tends to a value in the range [0-1]. When we consider the data for all the aggregates we may divide the α-range into two sub-ranges: [0,2] with sharp decrease of R_{Xu} and [2,10] with a nearly constant value of R_{Xu}.

In order to compare the different approximate methods we consider for each method ratio R_{method} / R_{Xu} with $R_{method} = C_{method,N}/(NC_{method,1})$. Tables 1 and 2 contain the performances of each method as the mean value of R (over 100 α-values) and the mean relative deviation (σ) between R_{method} and R_{Xu}. With the view to obtain significant calculations over different size parameter, we restricted the number of the primary particles by the values of 2, 4, 8 and 16. We also performed calculations in the case of 64 and 100 primary particles but with less number of size parameter (CPU time is too long) that why there are not include in the values of these tables.

Table 1: $0 < \alpha < 2$

configuration	linear						compact					
index	SiO_2		AlO_2O_3		TiO_2		SiO_2		AlO_2O_3		TiO_2	
method	mean	σ	mean	σ	mean	σ	mean	σ	mean	σ	mean	σ
CS	1.73	0.95	1.72	0.95	1.39	0.88	1.20	0.24	1.21	0.25	1.07	0.32
ERI	1.23	0.35	1.16	0.31	1.00	0.18	1.02	0.05	0.99	0.05	0.97	0.12
PBK	0.99	0.02	0.96	0.06	0.81[1]	0.21[1]	0.99	0.01	0.98	0.07	0.85[1]	0.17[1]
AD	0.60	0.45	0.57	0.48	0.57	0.53	0.56	0.50	0.53	0.52	0.51	0.57
R_{Xu}	2.47	2.32	2.56	2.45	2.85	3.08	3.70	4.12	3.82	4.34	3.97	5.06

(1) $0 < \alpha < 1$

Table 2: $0 < \alpha < 10$

configuration	linear						compact					
index	SiO_2		AlO_2O_3		TiO_2		SiO_2		AlO_2O_3		TiO_2	
method	mean	σ	mean	σ	mean	σ	mean	σ	mean	σ	mean	σ
CS	1.36	0.45	0.69	0.44	0.64	0.43	1.14	0.16	0.78	0.29	0.99	0.68
ERI	0.95	0.09	0.97	0.09	0.98	0.10	0.96	0.05	0.98	0.16	1.25	0.91
PBK	1.08	0.13	1.51	0.62	1.46[2]	0.56[2]	1.12	0.22	2.57	2.19	3.07[2]	4.26[2]
AD	0.94	0.10	1.07	0.16	1.07	0.08	0.94	0.07	1.05	0.12	1.44	1.27
R_{Xu}	1.19	0.25	0.87	0.18	0.83	0.18	1.40	0.50	0.76	0.38	0.64	0.43

(2) $1 < \alpha < 10$

4 CONCLUSION

As expected CS method is not appropriate. AD (anomalous diffraction) is a good approximation for $2 < \alpha < 10$. PBK is a good approximation for $0 < \alpha < 2$ but less efficient for material with high optical contrast. ERI seems the best for $0 < \alpha < 10$ except for chains of small primary particles. The last row of the Table 1 and 2 shows R_{Xu}. As it is

expected, this approximation is not acceptable for small primary particles ($0 < \alpha < 2$). The result becomes better for large primary particles, especially in the case of chains, but anyway ERI remains the best approximation.

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